The subsystem functional scheme:
The Armiento-Mattsson 2005 (AM05) functional and beyond

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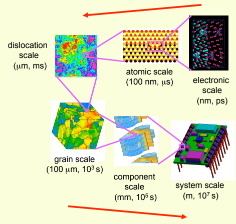
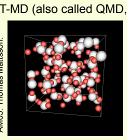
Density Functional Theory: The Underpinning of Predictive Multi-scale Efforts at Sandia



- Goal: Predict how materials age and perform under normal, adverse and extreme conditions.
- Method: Bridge length and time scales by using results from each scale as input on the next scale.
- Foundation: To get the fundamental processes right via DFT calculations at the electronic scale.
- Examples: DFT based EOS for continuum simulations. DFT investigations of Si and GaAs defects important for electronics modeling.

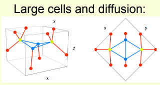
In addition to accuracy, also speed is very important

DFT-MD (also called QMD, AIMD, or FP-MD)


Snap shot of water simulation (64 molecules) done with AM05. Thomas Mattsson.

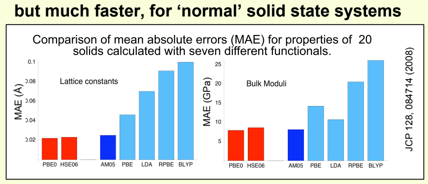
DFT is increasingly employed in quantum MD simulations of hundreds of atoms for tens of ps. This application demands functionals that are both accurate and fast. Every calculation with a temperature needs to be done with MD. Examples: Critical points and melting curves for EOS construction; Realistic calculations with water present.

Large cells and diffusion:


The Si ‹110› - split interstitial

Since all solid state DFT calculations uses periodic boundary conditions, large supercells are required for defect simulations in order to avoid uncontrolled interactions between defects. Calculating diffusion coefficients also require nudge elastic band type calculations where several copies of the same systems are needed.

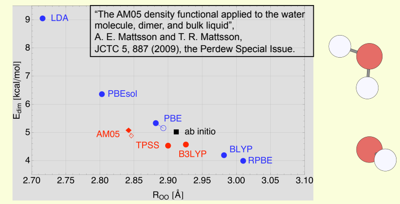
AM05 is as accurate as a hybrid, but much faster, for 'normal' solid state systems



GGA type functionals (blue) are one to three order of magnitudes faster to use than hybrids (red). AM05 has the same accuracy as hybrids for solids and thus enable accurate and fast DFT calculations of, for example, defects in semi-conductors. It also allows for the use of DFT-MD as an accurate tool in EOS construction.

Most important: AM05 proves that fast AND accurate is possible.

The binding energy and O--O distance of the water dimer



TPSS from Santra et al JCP 127, 184104 (2007)
B3LYP from Xu et al JPCA 108, 2305 (2004)
Best ab initio is CCSD(T)

AM05 works also for molecular systems, for properties that have small 'confinement' errors (see below). Note in particular the improvement over LDA.

AM05 works approximately as well as PBE for molecular chemical reactions

85 different chemical reactions between molecules from the G2 set:

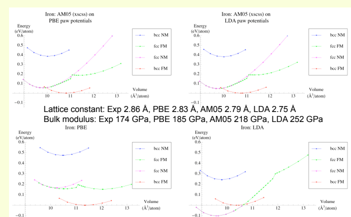
	B3LYP	BLYP	PBE	AM05
Mean Absolute Error	5.32 kcal/mol	7.30 kcal/mol	7.63 kcal/mol	8.08 kcal/mol

Note: AM05 is constructed without any reference to molecular or atomic systems.

Submitted. Preprint at arXiv:0908.1744
http://arxiv.org/abs/0908.1744

Spin AM05: Fe, Energy vs volume

"Implementing and testing the AM05 spin density functional", Ann E. Mattsson and Rickard Armiento, Physical Review B 79, 155101 (2009)



AM05 gives right bcc FM ground state, but uncharacteristically large errors in lattice constant and bulk modulus.

Van der Waals'

HAAS, TRAN, AND BLAHA — PHYSICAL REVIEW B **79**, 085104 (2009)

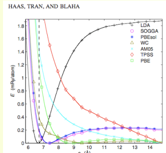


FIG. 3. (Color online) Total energy of graphite vs the lattice constant c (the interlayer distance is $c/2$). The in-plane lattice constant a was kept fixed at the experimental value (2.464 Å) for all values of c. The minima for the AM05 and TPSS functionals are either much larger than 15 Å or absent. The vertical dashed line represents the experimental lattice constant (c_0=6.71 Å).

TABLE III. Equilibrium lattice constant (in Å, a_0 for Ne and Ar, and c_0 for graphite). The Strukturbericht symbols are indicated in parenthesis.

Method	Graphite (A9)	Ne (A1)	Ar (A1)
LDA	6.7	3.9	4.9
SOGGA	7.3	4.5	5.8
PBEsol	7.3	4.7	5.9
PBE	8.8	4.6	6.0
WC	9.6	4.9	6.4
TPSS	>15	4.9	6.4
AM05	>15	>5.5	>6.7
Expt.	6.71[a]	4.47[b]	5.31[b]

[a]Reference 76.
[b]References 77–79.

Even though AM05 might be better off than other functionals since it contains no van der Waals', not even faulty, the fact remains that no functional does van der Waals' well.

AM05 is not the final answer: There is room for improvement.

Subsystem functionals

From general purpose functionals, to specialized functionals (and back).

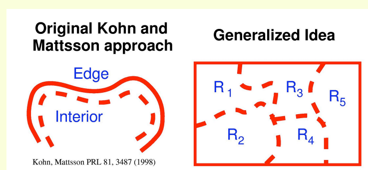
The *exchange-correlation energy per particle* is modeled in DFT.
LDA, GGA, meta-GGA, and AM05

$$E_{xc} = \int_V n(\mathbf{r})\,\epsilon_{xc}(\mathbf{r};[n])\,dV$$

Use specialized functionals in the different subsystems

Divide integration over V into integrations over subsystems

Every subsystem functional is designed to capture a specific type of physics, appropriate for a particular subsystem.

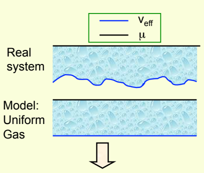


LDA: One subsystem. All parts of the system is assumed to be well described by the physics included in the uniform electron gas.

AM05: Two subsystems. Parts of the systems are either well described by a uniform electron gas or a surface jellium system.

Next functional: Three subsystems. Parts of the system are well described by either, the uniform electron gas, a surface jellium model, or a confined Mathieu gas model system.

The LDA functional



Assume each point in the real system contribute the amount of exchange-correlation energy as would a uniform electron gas with the same density.

Obviously exact for the uniform electron gas.

Basic concept and first explicit LDA published in 1965 (Kohn and Sham).

Compatibility: Benefit from using model systems

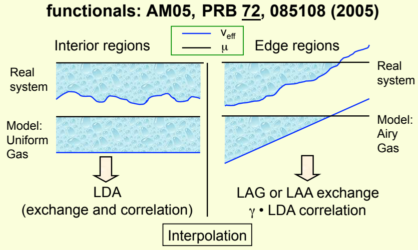
Jellium surface exchange and correlation energies
Example: r_s=2.07 (Al)

	σ_x	σ_c	σ_{xc}
Exact	2296	719	3015
LDA	2674	287	2961
PBE	2127	754	2881

In erg/cm²

PBE give more accurate individual exchange and correlation, but the sum is better described by LDA. Compatibility due to that LDA correlation is constructed from the remaining energy of the uniform electron gas.

General functional from subsystem functionals: AM05, PRB 72, 085108 (2005)



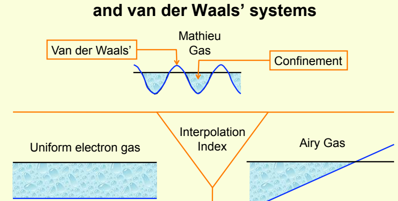
Two constants (one is γ above, one is in interpolation index) are determined by fitting to yield correct jellium surface energies.

The division into subsystems is done automatically via the interpolation index, which brings the specialized functionals back into one general functional.

Practical information about AM05

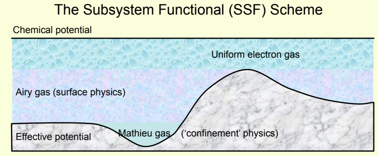
- AM05 can be implemented into any code that can run a GGA. Already implemented in VASP5 and many other codes.
- AM05 is as fast and easy to use as LDA and PBE.
- Subroutines (both for spin and non-spin) and information at http://dft.sandia.gov/functionals/AM05.html

A functional for confined and van der Waals' systems



Interpolation Index

The Subsystem Functional (SSF) Scheme



How to make a general functional using the SSF scheme:

- One specialized SSF for each type of physics.
- An interpolation index to decide how much of each type of physics should be included in each point of the system.

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